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PCT/NL00/00468

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 09 April 2001 (09.04.01)	
International application No. PCT/NL00/00468	**Applicant's or agent's file reference** 3887WO
International filing date (day/month/year) 03 July 2000 (03.07.00)	**Priority date** (day/month/year) 19 July 1999 (19.07.99)
Applicant LOONTJENS, Jacobus, Antonius et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

18 January 2001 (18.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Pascal Piriou

Telephone No.: (41-22) 338.83.38

Copy for the Elected Office (EO/EP)

PCT/NL99/00468

PATENT COOPERATION TRE

From the INTERNATIONAL BUREAU

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NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

OTTEVANGERS, S., U.
Vereenigde
Nieuwe Parklaan 97
NL-2587 BN The Hague
PAYS-BAS

Date of mailing (day/month/year)
30 June 2000 (30.06.00)

Applicant's or agent's file reference
P22073PC00

IMPORTANT NOTIFICATION

International application No.
PCT/NL99/00468

International filing date (day/month/year)
20 July 1999 (20.07.99)

1. The following indications appeared on record concerning:

[X] the applicant [X] the inventor [ ] the agent [ ] the common representative

Name and Address

State of Nationality

State of Residence

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[X] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

Name and Address

VAARKAMP, Marinus
Vleutenseweg 399
NL-3532 HH Utrecht NLX.
Netherlands

State of Nationality: NL

State of Residence: NL

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:
The above identified person has been added to the records as applicant/inventor for US only.

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer
A. Karkachi

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Form PCT/IB/306 (March 1994)

003385583

PATENT COOPERATION TREATY

REC'D 07 NOV 2000
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

15

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P22073PC00		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL99/00468	20/07/1999	22/07/1998
International Patent Classification (IPC) or national classification and IPC		
C10G65/08		
Applicant		
ENGELHARD CORPORATION et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

CORRECTED VERSION

Date of submission of the demand	Date of completion of this report
14/02/2000	03.11.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Falls, F Telephone No. +49 89 2399 8350

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00468

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-8 as originally filed

Claims, No.:

1-13 as received on 20/10/2000 with letter of 20/10/2000

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1, 3, 5, 6
	No:	Claims 2, 4, 7-13
Inventive step (IS)	Yes:	Claims
	No:	Claims 1, 3, 5, 6
Industrial applicability (IA)	Yes:	Claims 1-13
	No:	Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

1). Prior Art

Each of documents **US-A-3796654(D1), US-A-4190521(D2)** and **US-A-4036743(D3)** disclose a hydroconversion process of a HC feedstock, in which the S content is less than 50ppm, in the presence of a catalyst comprising a precious metal selected from those listed in claim 1, Ni and a metal oxide selected from those listed in claim 1; the components being present as a mixture on a support (see D1: Cl's 1, 4-6 & 19 and col. 15, table 1; D2: Cl's 1, 8 & 13 and col. 22, l. 11-18; and D3: Cl's 1, 13 & 18 and col. 20, l. 60-65).

2). Novelty (Art. 33(2) PCT)

It is considered that the teaching of each of these documents anticipate the subject-matter of claim 2. Claim 2 refers to a mixture in which the metal components may be present on a support, which is the teaching of D1-D3. As the process disclosed in each document involves the presence of hydrogen it is considered that in each case a process for the hydrogenation of S containing feedstock is in fact disclosed. Therefore the subject-matter of claim 2 lacks novelty against the disclosure of each of D1-D3.

Independent claims 1 and 3 refer to arrangements in which the 3 components are not mixed together; in which the precious metal and Ni are separate from each other. As this is not disclosed in any of the cited documents the subject-matter of these claims is novel.

At least one of the documents D1-D3 discloses the additional features of claims 4 and 7-13. Therefore the subject-matter of these claims also lack novelty.

3). Inventive Step (Art. 33(3) PCT)

In view of the prior art of D1-D3 an inventive step may only be recognized for the subject-matter of claim 1 or 3 if some advantage or effect is demonstrated for the separation of catalyst components as specified in these claims. There is no evidence in the application to establish that there is any advantage to choosing the order of treatment with the various catalyst components specified in independent claims 1 or 3 or for the order specified in dependent claims 5 or 6. Therefore there is no reason to suppose that the subject-matter of these claims contain an inventive step.

II

The application fails to meet the requirements of the convention in the following respects:

1). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D3 is not mentioned in the description, nor are these documents identified therein.

2). The unit inches (pg 7) have not been additionally expressed in metric units (Rule 10(1) PCT).

Int. pat. appln. no. PCT/NL99/00468
Our letter of October 20, 2000

EPO - DG 1

20 10 2000

(68) Claims

1. Process for the hydrogenation of a sulfur containing feedstock, having a sulfur content of less than 50 ppm, wherein the feedstock is hydrogenated in the presence of a precious metal catalyst, the precious metal being selected from platinum, palladium, rhodium, ruthenium, iridium, osmium and alloys thereof, such as platinum-palladium, and a nickel-catalyst, said process being carried out in such a manner, that the feedstock is contacted initially with the precious metal catalyst followed by contact with a metal oxide and the nickel catalyst, either in combination or sequentially, and wherein the metal oxide has been selected from the oxides of silver, lanthanum, antimony, bismuth, cadmium, lead, tin, vanadium, calcium, strontium, barium, cobalt, copper, tungsten, zinc, molybdenum, manganese and iron.

2. Process for the hydrogenation of a sulfur containing feedstock, having a sulfur content of less than 50 ppm, wherein the feedstock is hydrogenated in the presence of a precious metal catalyst, the precious metal being selected from platinum, palladium, rhodium, ruthenium, iridium, osmium and alloys thereof, such as platinum-palladium, and a nickel-catalyst, said process comprising contacting the feedstock with a mixture of precious metal catalyst, metal oxide and nickel catalyst, the previous metal catalyst being a supported precious metal catalyst and the nickel catalyst being Raney nickel or a supported nickel catalyst, and wherein the metal oxide has been selected from the oxides of silver, lanthanum, antimony, bismuth, cadmium, lead, tin, vanadium, calcium, strontium, barium, cobalt, copper, tungsten, zinc, molybdenum, manganese and iron.

3. Process for the hydrogenation of a sulfur containing feedstock, having a sulfur content of less than 50 ppm, wherein the feedstock is hydrogenated in the presence of a precious metal catalyst, the precious metal being selected from platinum, palladium, rhodium, ruthenium, iridium, osmium and alloys thereof, such as platinum-palladium, and a nickel-catalyst, said process comprising contacting the feedstock first with a mixture of precious metal catalyst and metal oxide, followed by contact with the nickel catalyst, and wherein the metal oxide has been selected from the oxides of silver, lanthanum, antimony, bismuth, cadmium, lead, tin, vanadium, calcium, strontium, barium, cobalt, copper, tungsten, zinc, molybdenum, manganese and iron.

4. Process according to claim 1-3, wherein the sulfur content of the feedstock is less than 10 ppm.

5. Process according to claim 1, wherein the feedstock, after hydrogenation with the precious metal catalyst and before the hydrogenation with the nickel catalyst is contacted with the metal oxide.

6. Process according to claim 1, wherein the feedstock is simultaneously contacted with the metal oxide and the nickel catalyst.

7. Process according to claims 1 or 3-6, wherein the precious metal catalyst is a supported catalyst.

8. Process according to claim 1-7, wherein the support of the precious metal catalyst is selected from silica, alumina, silica-alumina, titania, zirconia, zeolites, carbon, clay materials and combinations thereof.

9. Process according to claims 1-8, wherein the precious metal content of the catalyst is between 0.01 and 5.0 wt.%, calculated on the weight of the catalyst.

10. Process according to claims 1-9, wherein the nickel catalyst is Raney nickel or a supported nickel catalyst containing from 0.5 to 99 wt.% nickel.

11. Process according to claims 1-10, wherein the amount of precious metal catalyst ranges from 1 to 30 vol. % of the total system.

12. Process according to claims 1-11, wherein the weight ratio of nickel catalyst to metal oxide is between 20:1 and 1:20.

13. Process according to claims 1-12, wherein the feedstock is selected from petroleum distillates, resins and solvents.

15

PATENT COOPERATION TREATY

REC'D 18 SEP 2000
WIPO PCT

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P22073PC00		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL99/00468	20/07/1999	22/07/1998
International Patent Classification (IPC) or national classification and IPC C10G65/08		
Applicant ENGELHARD CORPORATION et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
14/02/2000	13.09.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Falls, F Telephone No. +49 89 2399 8350

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00468

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-8 as originally filed

Claims, No.:

1-11 as received on 13/07/2000 with letter of 13/07/2000

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1,2,5-11
Inventive step (IS)	Yes:	Claims	
	No:	Claims	3, 4
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

I

1). Each of documents US-A-3796654(D1), US-A-4190521(D2) and US-A-4036743(D3) disclose a hydroconversion process of a HC feedstock, in which the S content is less than 50ppm, in the presence of a catalyst comprising a precious metal selected from those listed in claim 1, Ni and a metal oxide selected from those listed in claim 1 (see D1: Cl's 1, 4-6 & 19 and col. 15, table 1; D2: Cl's 1, 8 & 13 and col. 22, l. 11-18; and D3: Cl's 1, 13 & 18 and col. 20, l. 60-65). It is consideed that each of these anticipate the subject-matter of claim 1. As the process disclosed in each document involves the presence of hydrogen it is considered that in each case a process for the hydrogenation of S containing feedstock is in fact disclosed.

Therefore the subject-matter of claim 1 lacks novelty against the disclosure of each of D1-D3 (Art. 33(2) PCT).

2). At least on ef the documents discloses the additional features of claims 2, 5-11. Therefore the subject-matter of these claims also lack novelty (Art. 33(2) PCT).

3). tjhere is no evidence in the application to estavblish that there is any advantage to choosing the order of treatment with the various catalyst components specified in claims 3 and 4. Therefore while the subject-matter of these claims appears to be new there is no reason to suppose that they contain an inventive step (Art. 33(3) PCT).

II

The application fails to meet the requirements of the convention in the following respects:

1). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D3 is not mentioned in the description, nor are these documents identified therein.

2). The unit inches (pg 7) have not been additionally expressed in metric units (Rule 10(1) PCT).

Int. pat. appln. no. PCT/NL99/00468
Our letter of July 13, 2000

Claims

1. Process for the hydrogenation of a sulfur containing feedstock, having a sulfur content of less than 50 ppm, wherein the feedstock is hydrogenated in the presence of a precious metal catalyst, the precious metal being selected from platinum, palladium, rhodium, ruthenium, iridium, osmium and alloys thereof, such as platinum-palladium, and a nickel-catalyst, said process being carried out in such a manner, that
- the feedstock is contacted with a mixture of precious metal catalyst, metal oxide and nickel catalyst,
- the feedstock is contacted initially with the precious metal catalyst followed by contact with the metal oxide and nickel catalyst, either in combination or sequentially, or
- the feedstock is contacted first with a mixture of precious metal catalyst and metal oxide, followed by contact with the nickel catalyst, and wherein the metal oxide has been selected from the oxides of silver, lanthanum, antimony, bismuth, cadmium, lead, tin, vanadium, calcium, strontium, barium, cobalt, copper, tungsten, zinc, molybdenum, manganese and iron.

2. Process according to claim 1, wherein the sulfur content of the feedstock is less than 10 ppm.

3. Process according to claim 1 or 2, wherein the feedstock is first hydrogenated using the precious metal catalyst, following which the feedstock is further hydrogenated using the nickel catalyst.

4. Process according to claim 3, wherein the feedstock, after hydrogenation with the precious metal catalyst and before the hydrogenation with the nickel catalyst is contacted with the metal oxide.

New page 10

5. Process according to claim 3, wherein the feedstock is simultaneously contacted with the metal oxide and the nickel catalyst.

6. Process according to claims 1-5,. wherein the precious metal catalyst is a supported catalyst, the support preferably being selected from silica, alumina, silica-alumina, titania, zirconia, zeolites, carbon, clay materials and combinations thereof.

7. Process according to claims 1-6, wherein the precious metal content of the catalyst is between 0.01 and 5.0 wt.%, calculated on the weight of the catalyst.

8. Process according to claims 1-7, wherein the nickel catalyst is Raney nickel or a supported nickel catalyst containing from 0.5 to 99 wt.% nickel.

9. Process according to claims 1-8, wherein the amount of precious metal catalyst ranges from 1 to 30 vol. % of the total system.

10. Process according to claims 1-9, wherein the weight ratio of nickel catalyst to metal oxide is between 20:1 and 1:20.

11. Process according to claims 1-10, wherein the feedstock is selected from petroleum distillates, resins and solvents.

FOR THE PURPOSES OF INFORMATION ONLY

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Title: Hydrogenation process

The invention relates to a process for hydrogenating a sulfur containing feedstock, such as resins, petroleum distillates, solvents and the like.

In hydrogenation often a problem presents itself in that the sulfur and/or sulfur components in the feedstock negatively affects the lifetime of the catalyst, especially of nickel catalysts. To avoid this problem much attention has been paid to the removal of sulfur compounds from the gaseous or liquid feedstock prior to the actual hydrogenation and/or dehydrogenation. Further, the presence of sulfur is quite often undesirable in view of the intended use of the hydrogenated material.

In general sulfur impurities are present in feedstocks as mercaptans or thiophenes, which can be hydrogenated to H_2S using a sulfidized Co-Mo catalyst. This method is also known as hydrodesulfurization (HDS). The H_2S formed may then, after separation and concentration, be processed to elemental sulfur in a conventional Claus process. This type of process is used for feedstocks containing large amounts of sulfur, i.e. more than about 0.1 wt.% of sulfur.

After conventional HDS treatment sulfur levels are usually in the range of about 500 ppm. Improved (or deep) HDS processes result in sulfur levels of about 50 ppm, whereas for further purified materials HDS processes have been developed resulting in sulfur contents after treatment of 10 ppm or less.

For some applications even these amounts of sulfur are still too high. In such a situation quite often use is made of a nickel catalyst. This catalyst has a dual function, as on the one hand the material is hydrogenated and on the other hand nickel reacts with the sulfur compounds. In the

course of time the nickel will deactivate, and finally will have to be replaced.

In EP-A 398,446 it has been proposed to use a hydrogenation or dehydrogenation catalyst based on at least one hydrogenation component and a metal oxide component, whereby the two components are present on a support as separate particles, preferably in absence of any direct contact between the metal oxide particles and the hydrogenation component particles.

This catalyst provides a good basis for the hydrogenation of various sulfur containing feedstocks. However, a disadvantage of this system resides therein, that the sulfur content of the feedstocks to be treated is limited, thus restricting the applicability.

In WO-A 9703150 a process is disclosed for the hydrogenation of sulfur containing feedstocks, wherein a feedstock having a sulfur content of preferably not more than 300 ppm is first contacted with a precious metal catalyst, followed by contact with a nickel catalyst. This process results therein that the deactivation of nickel is retarded considerably. This process shows a considerable advance in the art, however, for selected feedstocks and/or under specific circumstances further improvement has been considered desirable. More particular this system is suitable for light feeds, such as those that may be hydrogenated at temperatures below 200°C. For heavier feeds, requiring higher temperatures, this system is less suitable.

In the above process it may become a problem that the temperature window within which the process can operate efficiently is rather narrow. At low sulfur contents, quite often temperatures of over 200°C cannot be used effectively, although this would be advantageous in terms of hydrogenation activity.

It is a first object of the invention to provide a process for the hydrogenation of sulfur containing

feedstocks, having a widened temperature window, within which the process may be operated.

It is also an object to provide a process having a further improved tolerance for sulfur in the feedstock, i.e. which can have a longer life time before replacement becomes necessary. It is a further object to provide such a process wherein the deactivation of the catalyst system is retarded considerably.

It is also an object of the invention to provide a system that is very versatile in relation to the possibilities of regeneration and/or recovery of the catalyst components. Another object is to provide a system that may be used in situations where the sulfur content of the feedstock may fluctuate.

The invention is based on the discovery that the combined use of a precious metal catalyst, a nickel catalyst and a metal oxide results in an improved process, especially with respect to the objects stated above. It was found that especially at very low sulfur levels in feedstocks the effectivity of the removal of H_2S by nickel deteriorates.

The invention provides a process for the hydrogenation of a sulfur containing feedstock, having a sulfur content of less than 50 ppm, wherein the feedstock is hydrogenated in the presence of a precious metal catalyst and a nickel-catalyst, said process being carried out in such a manner, that

- the feedstock is contacted with a mixture of precious metal catalyst, metal oxide and nickel catalyst,
- the feedstock is contacted initially with the precious metal catalyst followed by contact with the metal oxide and nickel catalyst, either in combination or sequentially, or
- the feedstock is contacted first with a mixture of precious metal catalyst and metal oxide, followed by contact with the nickel catalyst.

In the broadest sense the process of the invention can be performed by the combined use of all three components,

wherein the precious metal will always be used at the start. In preferred embodiments the feedstock will first be hydrogenated using a precious metal catalyst, which is followed either by separate absorption (with metal oxide) and hydrogenation (with nickel) steps, or by a combined hydrogenation-adsorption step. It is, however, also possible to hydrogenate the feedstock using a combination (mixture) of precious metal and metal oxide, followed by nickel. This embodiment is not preferred, as it is more difficult to recover the precious metal catalyst.

It has been found that the present approach to hydrogenating hydrocarbon feedstocks that may contain varying amounts of sulfur impurities, provides a further improvement of the known systems. More in particular it has been found that this process has a high resistance against catalyst deactivation, especially for the treatment of heavy feedstocks, as the system remains stable and useful at higher hydrogenation temperatures, such as over 200°C.

Further the system is highly suitable for the removal of the last traces of sulfur, i.e. at level far below 10 ppm sulfur, for example 1 ppm or less. Conventional systems based on nickel do not result in sufficiently optimal economics of the process.

In the present invention various hydrocarbon feedstocks may be used. Preferred are petroleum distillates, resins, solvents and the like. It is possible to use these feedstocks directly, but it is also possible to use the product from a previous hydrodesulfurisation process, i.e a feedstock having a sulfur content reduced by deep HDS to less than 50 ppm. Surprisingly it has also been found that the system provides advantageous results in case of very low sulfur contents, i.e. below about 10 ppm.

The feedstock is hydrogenated over a conventional precious metal catalyst. Generally these are supported precious metal catalysts, containing from 0.01 to 5.0 wt.%, precious metal calculated on the weight of the catalyst.

Preferred amounts are between 0.1 and 2 wt %. The precious metals that may be used are platinum, palladium, rhodium, ruthenium, iridium and alloys thereof, such as platinum-palladium.

As support suitable supports for precious metal catalysts may be used, such as ceramic materials. Examples are silica, alumina, silica-alumina, titania, zirconia, zeolites, carbon, clay materials, combinations thereof and the like.

The metal of the metal oxide component will generally be selected from those metals that react with hydrogen sulfide to give stable metal sulfides. An enumeration of suitable metals has been given in the cited EP-A 398,446. Examples are silver, lanthanum, antimony, bismuth, cadmium, lead, tin, vanadium, calcium, strontium, barium, cobalt, copper, tungsten, zinc, molybdenum, manganese and iron. Preferred metals are zinc and manganese.

As indicated above, there are various possibilities for carrying out the present invention. With respect to all embodiments it is to noted that the steps can be carried out in separate reactors and/or in separate beds of the same reactor(s).

The hydrogenation of the feedstock over a nickel catalyst may be done using any nickel hydrogenation catalyst, such as Raney nickel or a supported nickel catalyst. Under the reaction conditions, the nickel will be mainly in the metallic form. The nickel content may range from as low as 0.5 wt.% to 99 wt.%. A preferred range is from 5 to 70 wt.%, calculated on the total weight of the reduced catalyst. Suitable support materials are the same as for the precious metal catalyst.

The skilled person can easily determine the relative amounts of the various components, depending on the various circumstances, such as sulfur content, type of feedstock and reactor configuration. As a guideline it can be indicated that of the total system (supported precious metal catalyst,

nickel catalyst and metal oxide), the amount of precious metal catalyst is preferably between 1 and 30 vol.%. Of the remainder of the system, the weight ratio of nickel catalyst to metal oxide ranges preferably between 20:1 and 1:20. The weight ratio of nickel, calculated as metal, to metal oxide (not being nickel oxide) ranges preferably between 1:10 to 100:1; outside these ranges either the effect on the life time of the system becomes too small to be attractive, or the activity decreases to a level that is economically less interesting.

The above ranges give a general guidance, but variations can be made to optimise the performance of the system.

An important advantage of the present invention resides therein, that it can be implemented in existing plants, without prohibitively high investments. This is especially important for the use of the invention in hydrogenation of solvents. The invention provides the possibility to use existing reactor volumes in an optimal manner, thus reducing costs, while at the same time improving the performance of the system, including the life time of the catalyst, especially when higher conversions are required.

The process of the invention may be carried out at the temperature, pressure and other reaction conditions usually encountered in conventional hydrogenation processes of hydrocarbon feedstocks. Temperatures may accordingly range from 150 to 300°C; pressures can be from 10 to 250 bar; and LHSV, H_2 to feed ratio, and the like are as usual. The amounts of catalyst and metal oxide depend on the amount of unsaturation that has to be removed, on the amount of sulfur and on the other reaction conditions. The skilled person is aware of all these variables and can easily determine the optimal values for the process.

The invention is further elucidated on the basis of the examples, which are intended as exemplary only, without limiting the scope of the invention.

EXAMPLES

In a trickle bed process a heavy solvent, boiling range 180 - 300°C, containing 8 ppm sulfur was hydrogenated at 30 bar hydrogen pressure. The degree of conversion of aromatics was determined using UV-absorbance at 273 nm.

In a trickle bed reactor a mixture of a supported nickel catalyst and zinc-oxide extrudates was present, on top of which a layer of supported platinum/palladium catalyst was applied.

The nickel catalyst was a 57 wt.% nickel on silica, in the form of 3/64" extrudates. The zinc-oxide extrudates were also 3/64". The precious metal catalyst was an 1.2 wt.% Pt/Pd (weight ratio 1/3) on silica-alumina spheres.

The respective amounts of catalyst were such that in the precious metal the LHSV was 35 hr^{-1} and in the mixture of nickel/zinc-oxide the LHSV was 10 hr^{-1}.

The reactor was operated in such a manner, that the decrease in the amount of aromatics in the product, due to deactivation, was kept constant by increasing the inlet temperature, until the maximum temperature of the reactor that can be used in reached (EOR: end of run temperature); in this case 275°C. The relation of sulfur dosage to the reactor and the inlet temperature required to meet the aromatics specification, is a measure for the properties of the catalyst and the resistance against deactivation.

In the following table the temperature versus sulfur dosage of the system of the invention has been given.

Sulfur dosage (Kg S/M^3)	Temperature (°C)
1	165
2	183
3	198
4	207
5	216
6	223
7	228
8	230
9	232
10	238
12	241
14	254

Claims

1. Process for the hydrogenation of a sulfur containing feedstock, having a sulfur content of less than 50 ppm, wherein the feedstock is hydrogenated in the presence of a precious metal catalyst and a nickel-catalyst, said process being carried out in such a manner, that
- the feedstock is contacted with a mixture of precious metal catalyst, metal oxide and nickel catalyst,
- the feedstock is contacted initially with the precious metal catalyst followed by contact with the metal oxide and nickel catalyst, either in combination or sequentially, or
- the feedstock is contacted first with a mixture of precious metal catalyst and metal oxide, followed by contact with the nickel catalyst.

2. Process according to claim 1, wherein the sulfur content of the feedstock is less than 10 ppm.

3. Process according to claim 1 or 2, wherein the feedstock is first hydrogenated using the precious metal catalyst, following which the feedstock is further hydrogenated using the nickel catalyst.

4. Process according to claim 3, wherein the feedstock, after hydrogenation with the precious metal catalyst and before the hydrogenation with the nickel catalyst is contacted with the metal oxide.

5. Process according to claim 3, wherein the feedstock is simultaneously contacted with the metal oxide and the nickel catalyst.

6. Process according to claim 1-5, wherein the metal oxide has been selected from the oxides of silver, lanthanum, antimony, bismuth, cadmium, lead, tin, vanadium, calcium, strontium, barium, cobalt, copper, tungsten, zinc, molybdenum, manganese and iron.

7. Process according to claims 1-6, wherein the precious metal catalyst is a supported catalyst, the support

preferably being selected from silica, alumina, silica-alumina, titania, zirconia, zeolites, carbon, clay materials and combinations thereof.

8. Process according to claims 1-7, wherein the precious metal content of the catalyst is between 0.01 and 5.0 wt.%, calculated on the weight of the catalyst.

9. Process according to claims 1-8, wherein the precious metal is selected from platinum, palladium, rhodium, ruthenium, iridium, osmium and alloys thereof, such as platinum-palladium.

10. Process according to claim 1-9, wherein the nickel catalyst is Raney nickel or a supported nickel catalyst containing from 0.5 to 99 wt.% nickel.

11. Process according to claim 1-10, wherein the amount of precious metal catalyst ranges from 1 to 30 vol. % of the total system.

12. Process according to claim 1-11, wherein the weight ratio of nickel catalyst to metal oxide is between 20:1 and 1:20.

13. Process according to claim 1-10, wherein the feedstock is selected from petroleum distillates, resins and solvents.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
P22073PC00		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/NL 99/ 00468	20/07/1999	22/07/1998
Applicant		
ENGELHARD CORPORATION et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. --

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
[redacted]T/NL 99/00468

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G65/08 C10G45/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 05739 A (SHELL INT RESEARCH) 12 February 1998 (1998-02-12) the whole document ---	1,3,5-13
A	EP 0 653 242 A (SHELL INT RESEARCH) 17 May 1995 (1995-05-17) the whole document ---	1,6-13
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A	WO 96 09360 A (MOBIL OIL CORP) 28 March 1996 (1996-03-28) --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 September 1999	17/09/1999

Name and mailing address of the ISA	Authorized officer
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Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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